TRACE METAL CONCENTRATIONS
AND THEIR RELATIONSHIP TO GEOLOGIC SOURCE

Based on a U.S. Geological Survey -
1968 Ground Water Study on the Ohio River Basin

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By
Mark Schipper
The Ohio State University
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Approved by:

Wayne Pettyjohn, Advisor
Department of Geology & Minerology

Contents

Note: The report, Ground-water Quality in the Ohio River Basin, by Deutch, Pettyjohn, Wallace, and Jordan has not been published at this time and is not available to the general public.

INTRODUCTION

In the late 1960's, the U.S. Geological Survey conducted a ground-water survey of trace elements throughout the Ohio River Basin (Ohio, Indiana, Kentucky, Tennessee, Pennsylvania, and West Virginia). The sample points were distributed throughout 12 sub-basins. Eighty samples were collected and analysed for sixty-three trace elements although only twenty-one of these trace elements occurred consistently in detectable concentrations. Unfortunately, the U.S.G.S. report was never published. This report describes the range in concentration, maximum, minimum and mean values of the elements.

The samples were taken from varied geologic sources (aquifers) from wells that ranged widely in depth. The sources include Pennsylvanian, Mississippian, Devonian, Silurian and Ordovician age rocks as well as several types of glacial deposits (outwash sand and gravel, glacial drift, and lenses of gravel in till). Alluvial aquifers served as a source ofr three samples.

It is the purpose of this report to investigate the possible relationships between geologic source and trace element concentrations.

ROCK TYPE AND NUMBER OF WATER SAMPLES

Ordovician

(2 samples) The lithologic units consist of thin bedded limestones, which range from sandy muddy to clean skeletal, interbedded with shales and clays. There is some sandstone in the middle to lower Ordovician.

Silurian

(3 samples) The Niagaran Fm. is a well marked lithologic unit of limestones and shales, which extends from the top of the Clinton Fm. to the base of the Onendaga salt group. (1 sample) The Bass Island Dolomite, Upper Silurian in age, is unconformable above the Niagara group and lies below the Oriskany formation.

Devonian

(1 sample) The Columbus and Delaware limestone is Middle Devonian in age. The Columbus limestone is one hundred and five feet thick and underlies the Delaware limestone, which is thirty-six feet thick. The Olentangy shale overlies the Delaware limestone.

Mississippian

(3 samples) Poncono Group. In south central Pennsylvania, the Poncono group consists of one thousand six hundred feet of sandstone and pebble conglomerate beds. The Berea Sandstone is included in this group and consists of coarse, reddish brown micaceous sandstone. Shale, siltstone and coal also occur in this group.

(1 sample) Conneaunt Fm. This is Mississippian in age and outcrops in Northwestern Pennsylvania.

(1 sample) Cuyahoga Fm. This is a member of the Poncono Group, which outcrops in Ohio and Western Pennsylvania. It consists of conglomerate, sandstone, and shale. It underlies the Logan Fm.

(1 sample) Maxville Limestone. This unit is Upper Mississippian in age. It underlies the Pottsville Fm. of Pennsylvanian age, and overlies the Logan Fm. After deposition atop the Logan, extensive erosion occurred which left the Maxville Limestone only in small isolated particles.

Pennsylvanian

(1 sample) Dunkard Fm. Upper Pennsylvanian to Permian in age, the Dunkard consists of sandstone, shale and siltstone.

(7 samples) Conemaugh Fm. Consisting of sandstone, freshwater limestone, red shale, marine shale, and coal, the Conemaugh Fm. differs from the Allegheny Fm. and Pottsville Fm. in that it contains a greater number of red beds.

(4 samples) Allegheny Fm. The Allegheny Fm. contains six mappable coal beds and consists of an alternating sequence of shale, sandstone, limestone, and clay.

(9 samples) Pottsville Fm. Middle Pennsylvanian in age, the Pottsville is two hundred and forty feet thick. The upper third consists of a highly variable sequence of clays, shales, and sandstones. The lower one hundred and sixty feet is mostly thick sandstones with a few thin coal beds.

Glacial

(19 samples) Sand and gravel, contains rock debris from the Canadian Shield as well as Devonian, Mississippian, Pennsylvanian, and Permian rock types. There is some interbedded silt and clay, but the gravel, mostly out-wash by origin, is fairly clean and well sorted.

(3 samples) Alluvium. The water sources within the alluvium are probably thin sand and gravel lenses.

QUANTITATIVE METHODS

The analytical data were divided into sub-groups according to age and/or source. The minimum, maximum, median, and mean concentration values for each element were then calculated. These values appear in Table 1.

The calculation of mean value presented two major problems. First, non-detectable values had to be dealt with. The choice existed to assign non-detectable concentrations a zero value, or to ignore them. Statistical Methods in Geology (1972) suggested the following equation:

$$\sum_{1}^{n} \frac{S_1 + S_2 + S_3 + S_n}{n} + \sum_{1}^{k} \frac{S_1 + S_2 + S_3 + S_k}{k}$$

Where concentrations reported as non-detectable are considered to have a value of zero and n = total number of samples

S_1 = concentration of sample 1

S_2 = concentration of sample 2

S_3 = concentration of sample 3

S_n = concentration of the nth sample

and concentrations having non-detectable concentrations are not considered.

k = total number of samples

S_1 = concentration of sample 1

S_2 = concentration of sample 2

S_3 = concentration of sample 3

S_k = contration of kth sample

If non-detectable values were treated as zeros, the mean would be lowered, whereas if non-detectable were ignored, the mean value would be increased. This equation establishes some kind of average between the value treatments.

The numerical form of the data presented the second problem in determining a mean. Roughly half of the concentrations were reported as less than x, where x represented the upper limit of detection. These are non-parametric data and can not be incorporated in a mean value concentration. After all, less than one thousand is quite ambiguous, because this yields one thousand possible concentration values. Where this particular problem arose, the calculation of a mean value was not performed.

The minimum, maximum, and median values were determined in every case.

These data must be examined with caution. Reliability and exactness of detection methods varies between elements. For some elements. very exact values can be determined, whereas some elements are very difficult to determine quantitatively with precision. The analyst is limited by his equipment, his procedure, and his technique. Hopefully, though a fairly good idea of concentration ranges for a wide variety of elements can be derived from this report.

DESCRIPTION OF CONCENTRATIONS AND STATISTICAL VALUES

Aluminum

Ground-water samples from the Ohio River Basin include 80 analyses and 80 aluminum values. Concentrations range from a low of non-detectable to a maximum of .530 mg/l.

Three wells yielded non-detectable for aluminum. The wells were in Licking, Perry, and Fairfield counties in Ohio. The Licking County well tapped the Cuyahoga Fm. of Mississippian age. Pottsville and Allegheny sandstone and shale of Pennsylvanian age provided the non-detectable source for the Perry County well. Finally, the third non-detectable value originated from glacial outwash gravel in Fairfield County, Ohio.

The maximum concentration, .530 mg/l, was from the Conemaugh Fm. of Pennsylvanian age, with the water sample probably drawn from a sandstone, although the Conemaugh contains varied lithologies including claystones, shales, freshwater limestones, and some coal.

The mean value of the entire suite of samples was .079 mg/l.

The analytical data do not appear to indicate any particular rock type, geologic age, or geographic locality in which the concentrations are significantly above or below the mean. More importantly, not a single sample was unusually high, since the maximum concentration is considerably less than 1 mg/l.

Aluminum concentrations are generally very low in uncontaminated waters as indicated by the above data. Aluminum never appears in nature as a pure metal, although many of its salts are quite soluble. Other aluminum salts, however, are quite insoluble and consequently aluminum does not occur in surface waters for long because it precipitates and settles or is absorbed as aluminum hydroxide,

aluminum carbonate, etc.

Even if aluminum were to be found at much higher concentrations, its bad effects on human health would be negligible, because the excess aluminum is excreted with feces (Browning, 1963). The U.S. Public Health Service has not set a recommended limit for drinking water. Also, this element apparently is not essential to good health.

Concentrations of aluminum in water may become important to industries. Concentrations as low as .05 mg/l may cause problems in laundries and mineral water plants (McKee & Wolfe, 1963).

Barium

Eighty barium analysis were performed. Concentrations range from a low of .004 mg/l to a maximum of .770 mg/l. The lowest concentration was from a well tapping the Bass Island Group, a limestone of Silurian age, located in Union County, Ohio. The maximum was from the Pottsville Fm. of Pennsylvanian age, obtained from a well in McDowell County, West Virginia, The median value of the eighty barium analysis was .115 mg/l and the mean was .185 mg/l. The three highest mean values by source were sand and gravel (200 mg/l), Ponoco Fm., Mississippian (.212 mg/l), and Allegheny & Pottsville, Pennsylvanian (.290 mg/l). The three lowest mean values by geologic source were: Bass Island Fm., Silurian (.004 mg/l), the Ordovician (.025 mg/l), and the Tertiary and Cretaceous (.014 mg/l).

The data indicates that barium concentrations from limestone and dolomite sources are lower than the mean. $BaCO_3$, Barium carbonate, is highly insoluble. The highest values seemed to come from sand stone units within Pennsylvanian and Mississippian rocks, as well as from glacial sand and gravel. But the significance of small concentration differences within a suite of concentrations which

are consistently low (all less than 1 mg/l) to begin with, raises the question whether the observed trends exist and also whether such differences really matter.

Barium is not common in natural surface or ground waters. Many of its salts are soluble but the carbonate and sulfate are highly involuble; consequently, any Barium discharged into natural waters will be quickly precipitated and removed by absorbtion or sedimentation (McKee & Wolfe, 1963).

The U.S. Public Health Service has set a mandatory upper limit of 1 mg/l for drinking water. Barium presumably has toxic effects on the heart, blood vessels and nerves (Derby, Hopkins, and Gullans, 1960). All eighty barium concentrations fell below 1 mg/l. The data, therefore, seem to indicate that barium does not create a health problem in natural ground-waters of the Ohio River Basin.

Beryllium

Eighty ground-water samples showed consistently low concentration values. Concentrations ranged from a low of less than .0002 mg/l to a high of less than .012 mg/l. Seven samples possessed the minimum value, less than .0002 mg/l. Three were from Pennsylvanian rocks, three from Mississippian rocks, and one was from a Tertiary and Cretaceous source. The minimum values came from well samples taken in Kentucky (3 samples), Tennessee (3 samples), and West Virginia (1 sample). It is interesteing to note that all the minimums came from sample points south of the line created by the Ohio River, which cuts the basin into a north and south area of roughly equal size. All the minimums came from rocks of Mississippian age or younger. The maximum value, less than .012 mg/l, was from sand and gravel outwash located in Trumbull County, Ohio. A well in Muhlenburg County, Kentucky possessed the same value, but its source was not stated.

The median value of the entire suite was less than .002 mg/l and sixteen samples possessed this value.

The total value range, less than .012 to .0002, shows that the difference from highest to lowest value is less than a hundredth of one part per million. Certainly the significance of the inter-sample differences can be questioned. Despite this, a good idea of concentration of beryllium in natural waters in the Ohio River Basin can be obtained from the data.

Beryllium is a relatively rare element, found chiefly in the mineral beryl, and is not likely to occur in natural waters. Although the chloride and nitrate are very soluble and the sulfate moderately so, the carbonate and hydroxide are almost insoluble (McKee & Wolfe, 1963).

Pomelee reports that there was no indication that beryllium in any form is harmful when taken internally through the digestive tract (Pomelee, 1953). On the other hand, beryllium dust in air has caused pulmonary disease to workers exposed to its dust. Observing the eighty concentration values of beryllium from the Ohio River Basin, two things become evident, that the values are consistently low and that even if the highest value, less than .012 mg/l, was multiplied by a factor of 1,000 it would not be harmful to health if ingested through domestic use.

Boron

Throughout the entire suite of eighty ground-water analysis for the Ohio River Basin, boron showed a relatively wide r nge in value with a high of .53 mg/l and a minimum of .007 mg/l. The highest concentration was from a well tapping gravel outwash in Trumbull County, Ohio. The minimum value, .007 mg/l, is possessed by three well analysis; a well tapping sand and gravel in McKracken County, Kentucky, a well tapping of the Pennsylvanian age in Wayne County, Kentucky,

and thirdly a well located in Trigg County, Kentucky, with unidentified source. The maximum concentration from a known source was .530 mg/l, however ground-water analysis of an unknown source in Muhlenburg County, Kentucky yielded a concentration value of .570 mg/l. It is interesting to note that these two sources also produced the maximum values for beryllium. In addition, it is surprising that two of the three boron minimums came from sources which were also Beryllium minimums. Possibly, a positive correlation exists between boron and beryllium concentration values.

The mean concentration of boron for the entire suite of minerals is .086 mg/l. The median concentration is .051 mg/l.

The analytical data does not appear to indicate any rock type, geologic age, or geographic locality in which concentrations are significantly above or below the mean.

Boron is never found in nature in its elemental form, but occurs as sodium borate (borax) and as calcium borate (colemanite). It is found in natural waters of Southern California and Italy.

There is no evidence that boron performs any vital function in human or animal nutrition. Also, boron in drinking water is not generally regarded as a hazard to human beings. Goudy and others have reported that boron concentrations up to 30 mg/l are not harmful in drinking water (Goudy, 1936).

Boron can cause a problem when its concentration exceeds .5 mg/l in irrigation water. It causes deleterious effects on such crops as peaches, grapes, and cherries. Crops such as wheat and corn can not grow well at concentrations exceeding 2 mg/l (McKee & Wolfe, 1963).

With respect to domestic and agricultural use, the ground-water in the Ohio River Basin does not possess a harmful amount of boron. Aside from this,

however, a few high concentrations exist (above .5 mg/l). This seems odd when the rarity of boron in its elemental form is considered. The high of .530 mg/l came from a sand and gravel source. Higher than usual concentrations of boron in this type of geologic source bears two possible explanations; that the great amount of inter-granular surface area possessed by a sand and gravel mixture presents a large amount of rock surface for ion exchange, thus allowing a relatively large amount of material to go into solution, and the ground-water movement through gravel is fairly rapid and thus sand and gravel aquifers are more prone to contamination by foreign elements via rapid ground-water movement.

The use of borates aor fertilizer and its subsequent rapid movement by ground-water may provide a possible explanation for high boron concentrations, especially in sand and gravel aquifers.

Chromium

Ground-water samples from the Ohio River Basin include 80 analysis and 80 chromium values. Concentrations range from a low of less than .0006 mg/l to a maximum of less than .040 mg/l. The lowest was from a well tapping a Tertiary and Cretaceous source in Carlisle County, Kentucky. In addition, a value of less than .0007 mg/l came from two wells. One tapped sand and gravel and was located in Pike County, Ohio. The other tapped Mississippian rocks and was located in Delaware County, Ohio. The highest value came from an unstated source in Muhlenburg County, Kentucky, a well which supplies the drinking water to Drakesboro, Kentucky. This well also had maximum values for boron, beryllium, and iron. The highest value for a known source was less than .030 mg/l and was possessed by two wells; one tapped sand and gravel in Trumbull County, Ohio. The other tapped Alluvium in Allegheny County, Pennsylvania. The median value for the entire suite was less than .006 mg/l.

If the median values that were obtained from sample subgroups differentiated by geologic source are examined, it is found that from source to source, no geologic source median value varies from the median of the entire sample suite, less than .006 mg/l, by more than .020 (two hundredths of one part per million). Yet this is nearly a full magnitude of ten, if one considers that the median value is 6 thousandths of one part per million.

These value differences seem insignificant, but when the USPHS limit for hexevolent chromium (.050 mg/l) is considered, it is found that ten percent of the chromium analysis are .020 mg/l or greater, and possibly these values suggest that problems do exist with chromium in natural ground-waters.

But, on the basis of toxicity to humans, it is difficult to understand why the USPHS has placed such a low limit on chromium for domestic waters. A family in New York has been drinking water from their private well that possesses a chromium concentration of greater than 10.0 mg/l, for a period of years - with no ill effects (McKee & Wolfe, 1963).

Cobalt

Cobalt concentrations ranged from a high of less than .080 mg/l to a low of less than .0006 mg/l. The high was from an unnamed source in Muhlenburg County, Kentucky. The next highest source, less than .050 mg/l, came from rock of Pennsylvanian age located in Daylight, Indiana. The low, less than .0006 mg/l, was from the Allegheny Fm. of Pennsylvanian age and was located in Fayette County, Pennsylvania. The next lowest concentration, less than .0008 mg/l, was from the Pottsville Fm., Pennsylvania. The Allegheny Fm., Pennsylvanian, had the third lowest value, .0009 mg/l. The Pennsylvanian sources accounted for both the highest and lowest concentration values. The Pottsville and Allegheny Fms.,

specifically, accounted for the three lowest cobalt values.

The median value for the entire suite of samples was less than .008 mg/l.

The highest concentration value, less than .080 mg/l, came from the same well that produced the maximum for boron, beryllium, iron, and chromium. The well, located in Muhlenburg County, Kentucky, has no stated geologic source.

Solutions containing cobaltous ions (Co^{++}) are relatively stable, but cobaltic ions (Co^{+++}) are powerful oxidizing agents and consiquently they are unstable in natural waters (McKee & Wolfe, 1963).

Traces of cobalt are essential to both plant and animal growth. Cobalt concentrations of greater than 2 mg/l stunted the growth of plants and caused withering. The ingestion of soluble cobalt salts in sufficient concentrations by humans produces nausia and vomiting by local irritation. Not enough is known at present to determine a safe concentration of cobalt in drinking water, however the ingestion of .1 to .25 mg/day does not appear to have any harmful effects (McKee & Wolfe, 1963). Concentrations of cobalt found in the Ohio River Basin ground-water study appear well below a problem level. The highest concentration was less than .080 mg/l.

Copper

Ground-water samples from the Ohio River Basin include eighty analysis and eighty copper values. Concentrations range from a high of .440 mg/l to a low of less than .001 mg/l. The high concentration came from a well tapping rock of Tertiary and Cretaceous age located in Carlisle County, Kentucky. Another well that tapped a sand and gravel source in McKracken County, Kentucky produced a copper value of .250 mg/l. The low value, .001 mg/l, was shared by four wells: outwash sand and gravel located in Madison County, Ohio, glacial drift from a

source west of Coney, Kentucky, rocks of Mississippian age located in Wilson County, Tennessee, and finally a well tapping the Pottsville Fm. of Pennsylvanian age located in Harlan County, Kentucky.

The median concentration value was .004 mg/l.

The highest concentration, .440 mg/l, is two magnitudes of 10 greater than the median of .004 mg/l.

The chloride, nitrate and sulfate of divalent copper are very soluble, but the carbonate, hydroxide, and oxide are not. Cupric ions, when introduced into natural waters with a ph. above 7 will quickly precipitate in either the hydroxide or as copper carbonate, $CuCo_3 \cdot Cu(OH)_2 \cdot 2H_2O$. For this reason, copper ions should not be expected in natural surface or ground-waters, especially in limestone regions where very hard water is expected to be found (McKee & Wolfe, 1963).

Copper is not considered a cumulative systamatic poison. It is considered essential, in trace amounts, to health. Surprisingly, it is not toxicity but rather taste which imposes restrictions on the amount of copper in drinking water. As little as 4 mg/l can make water unpalatable. The USPHS has set a recommended limit of 1 mg/l for domestic supplies.

Copper, although apparently not harmful to humans, has very deleterious effects on vegetation and aquatic life. A limit of .02 mg/l for fresh water aquatic life has been suggested. Additionally, a limit of .1 mg/l has been suggested for water used in irrigation (McKee & Wolfe, 1963).

Four of the eighty copper values surpassed the suggested upper limit for aquatic life. Two values violated the irrigation limit. No values surpassed the drinking water standard.

Upon inspection of the data, three wells are found with concentrations of

.02 mg/l or greater. It is not wholly unreasonable to suppose that these wells are contaminated, possibly by leakage from water sources which have been treated with vegetation inhibiting copper sulfate, pipe corrosion, or industrial effluents. The causes for these high concentrations could also be natural, although natural contamination, at least in this case, is inexplicable.

Iron

Iron displays a very wide range in concentration for the eighty iron analysis performed in the Ohio River Basin study. Concentrations range from a low of .004 mg/l to a high of 11 mg/l. The lowest concentration was from a well tapping the Pottsville Fm. of Pennsylvanian age located in Wayne County, Kentucky. Two other low values of .005 mg/l came from a well tapping a Pennsylvanian source located in Wolfe County, Kentucky and one tapping a Tertiary and Cretaceous source in Carlisle County, Kentucky. The highest value came from a well in Muhlenburg County, Kentucky. No geologic source was stated on the sample sheet. This well also possesses the maximum concentrations of beryllium, cobalt, chromium, and boron. A value of 4.5 mg/l was found in a well tapping sand and gravel in Allegheny County, Pennsylvania.

A well tapping Bass Island Limestone, Silurian age, had a value of 3.8 mg/l.

The median for iron was .230 mg/l.

Iron is essential to good health, and an average diet contains 16 mg/day. Therefore, even the highest value found in the Ohio River Basin, 11 mg/l, would not be toxic, even over a long period of time. The problem which exists with iron, however, is the bad taste associated with it in waters containing more than .1 mg/l. For esthetic reasons, the USPHS has established .3 mg/l as the limit for domestic water supply. Over half of the eighty wells tested surpassed this limit. In respect to use for drinking water, a definite problem exists in the Ohio River Basin.

Above .3 mg/l, iron will cause staining of laundry. High iron concentrations will tend to cause livestock to drink less, hence milk production is affected (McKee & Wolfe, 1963).

The Pennsylvanian and sand and gravel sources had the highest mean concentrations for iron, 1.0 mg/l. Perhaps the sand and gravel sources, glacially derived, contain a large amount of iron bearing rock transported from Canadian Shield sources to the north. The high concentrations in the Pennsylvanian series might be attributable to leaching of soluble iron salts from soil and rocks including acid mine drainage which might represent at least some localized causes of high iron concentrations in the Pennsylvanian source wells. Also, wells tapping limestone sources usually possessed concentrations above the mean.

Lead

The concentration of lead throughout the entire suite of eighty analysis was low, with all concentrations well below 1 mg/l. The highest concentration was .030 mg/l and came from a Columbus and Delaware limestone source, located in Delaware County, Ohio. The second highest concentration, .029 mg/l, originated from the Pottsville Fm. of Pennsylvanian age from a well in Somerset County, Pennsylvania. The lowest concentration was .001 mg/l from a Pennsylvanian source in Leslie County, Kentucky.

The median concentration was less than .005 mg/l.

The third highest value for lead was less than .025 mg/l. This is five thousandths of 1 mg/l less than the maximum lead concentration of .030 mg/l. This third highest value came from a well of unstated source in Muhlenburg County, Kentucky which also had the maximum for iron, cobalt, boron, beryllium, and chromium.

No median values for any specific geologic sources differed from the median for all eighty samples by more than five thousandths of 1 part (.005) per million. No trends were apparent.

Lead does not persist for long in natural waters, owing to the fact that the carbonate and hydroxide are insoluble and the sulfate sparingly so (McKee & Wolfe, 1963).

Lead is a cumulative poison which tends to accumulate in the bone. Lead is not considered essential to human nutrition and health (McKee & Wolfe, 1963).

Since the public is being subjected to more and more ingestion of lead from food, inhaled atmosphere and industrial urban areas, the USPHS limit for lead has been set at .05 mg/l. No lead analysis equalled or surpassed this value, but a few values were within 2 hundredths (.02 mg/l) of it.

Galena, Pbs, often associated with limestone, and possibly present in significant amounts in the Ohio River Basin sands and gravels, might be responsible for the higher concentrations among the lead values. Limestone associated ground-waters, on the other hand, are expected to have low lead values because of the high insolubility of lead carbonate. At any rate, a problem does not seem to exist.

Lithium

Lithium values were obtained for eighty ground-water samples from the Ohio River Basin. The concentrations ranged from a low of .0001 mg/l to a high of .095 mg/l. The low concentration came from a well tapping a Tertiary and Cretaceous source located in Carlisle County, Kentucky. A concentration of .0002 mg/l was found from an alluvium source located in Washington County, Ohio. An Ordovician source in Jessmine County, Kentucky produced a value of .0005 mg/l.

Three values were .090 mg/l or above. The maximum, .095 mg/l, came from a well of unreported source in Muhlenburg County, Kentucky. This well also had the highest value for beryllium, boron, chromium, cobalt and iron, and the third highest value for lead. A value of .090 mg/l was found in a sand and gravel source in Trumbull County, Ohio, which also had the second highest value for boron. The Bass Island limestone, of Devonian age, located in Union County, Ohio also had a value of .090 mg/l.

The median concentration for lithium was .006 mg/l. No particular geologic source values seemed to deviate from the mean by a significant amount.

Lithium is a very chemically active element, and does not occur in elemental form in nature. Elemental lithium must be protected from oxygen and water, or it quickly reacts. Below 1 mg/l, lithium presents no problems for both drinking and irrigation water. Hibbard suggests a limit of 5 mg/l for drinking water (Hibbard, 1934). No lithium values in the Ohio River Basin were found to be greater than .1 mg/l.

Manganeese

Manganeese concentrations obtained in the Ohio River Basin study ranged from a low of .0004 mg/l to a high of 3.60 mg/l. The range of manganeese is quite similar to the range of iron. The low value, .0004 mg/l, came from a well tapping Tertiary and Cretaceous rocks in Carlisle County, Kentucky. This well also produced the second lowest concentration value for iron, .005 mg/l. The next lowest value, .0006 mg/l, was from the Pottsville Fm. of Pennsylvanian age, and came from a well in Wayne County, Kentucky. This well possessed the lowest iron concentration, .004 mg/l. The highest concentration, 3.6 mg/l, came from a sand and gravel source in Allegheny County, Pennsylvania, a source which also

produced the second highest iron value, 4.5 mg/l. A positive correlation exists between iron and manganeese.

The median concentration value of manganeese was .060 mg/l. No trends were obvious. Sand and gravel sources and Pennsylvanian age sources appear to possess the highest manganeese values. These two geologic source types also possess the lowest manganeese concentration values.

Manganeese metal is not found pure in nature, but its ores are common and widely distributed. Like iron it occurs in divalent and trivalent form. In surface waters manganeese is seldom found above a concentration of 1.0 mg/l, but in ground-water subject to reducing conditions, manganeese can be leached from the soil and occur in high concentrations (McKee & Wolfe, 1963).

Manganeese can not be considered a physiological hazard because the normal dietary intake is 10 mg (Rothstein, 1953), far higher than the amount that would be tolerated esthetically in drinking water (McKee & Wolfe, 1963).

Concentrations of manganeese above .5 mg/l are reported to impart bad taste, cause staining of laundry, and cause brewing problems. The W.H.O. has set the excessive limit of manganeese at .5 mg/l. The USPHS has recommended a limit of .05 mg/l in domestic supplies. Forty-two of the eighty manganeese values surpass the recommended limit. Eight values (10%) of the eighty values surpass the W.H.O. excessive limit. Manganeese, like iron, seems to be a major problem in Ohio River Basin ground-waters.

Molybdenum

Eighty analysis provided eighty concentration values for molybdenum. The highest value was .037 mg/l and the lowest was .0001 mg/l. The highest concentration came from a sand and gravel source located in Madison County, Ohio. The Bass Island Fm., of Silurian age, possessed the next highest value, .023 mg/l.

Sand and gravel yielded the third highest value, .022 mg/l. The four lowest molybdenum values originated from Pennsylvanian age sources, and specifically from the Allegheny and Pottsville Fms. The low value, .0001 mg/l, was from the Pottsville Fm., Pennsylvanian age, from a well located in Somerset County, Pennsylvania.

The median value for molybdenum was less than .005 mg/l. Both the Pennsylvanian and Mississippian sources had a median below the median for all eighty samples, with their median values being less than .001 and .001 respectively. Glacial gravel had the highest median value, less than .010 mg/l. Sand and gravel had a median of less than .004 mg/l. The Silurian sources of Niagaran age possessed the second highest source median, .009 mg/l.

Molybdenum is not widely distributed in nature, although it occurs in the minerals molybdenite, MOS_2, and Wolfenite, $PbMoO_4$. It is not considered to be significant in water pollution and no domestic standards have been set.

Molybdenum is essential to health of both plant and animal. Concentrations above 50 mg/l have toxic effects to soybeans and clover (McKee & Wolfe, 1963). High concentrations in plants (above 50 mg/l) has caused serious problems to cattle (Ferguson, Lewis, Watson, 1943).

It is difficult to determine whether the concentration differences of Molybdenum encountered in the Ohio River Basin are significant. The high concentrations found in sand and gravel seem worth mentioning. They are possibly due to leaching of molybdenum bearing rocks in the sand and gravel aquifers. These molybdenum bearing rocks can possibly be linked to a Canadian Shield source, with glacial transport as the vehicle of movement, but many other factors could be responsible such as: the high granular surface area of a gravel aquifer, and/or the rapid rate of ground-water flow within a gravel aquifer.

Nonetheless, molybdenum in its reported concentrations in the Ohio River Basin apparently poses no threat.

Nickel

Nickel concentrations were obtained for eighty ground-water samples. Concentrations ranged from a hgih of less than .040 mg/l to a low of less than .0007 mg/l. The high concentration came from an unreported geologic source in Muhlenburg County, Kentucky. This well, which serves as the public water supply for the city of Drakesboro, Kentucky also had the highest concentrations of boron, beryllium, chromium, cobalt, iron, lithium, and lead. The third highest concentration was less than .020 mg/l, and was taken from a well in Trumbull County, Ohio tapping a sand and gravel source. This same well possessed the second highest cobalt concentration. The second highest concentration, less than .025 mg/l, was taken from a Pennsylvanian source in Daylight, Indiana.

The low, less than .0007 mg/l, was shared by two wells, both of the same source, the Pottsville Fm., Pennsylvanian age. Both wells were located in Pennsylvania.

The median concentration of nickel was less than .006 mg/l. No particular source median varied significantly. The highest source median for a source containing more than three separate analysis was less than .007 mg/l for the Niagaran Fm., Silurian age. The lowest median value was less than .008 mg/l from the Pottsville Fm., Pennsylvanian age.

Elemental nickel is not soluble in water, but many of its salts are. No data of the toxicity of nickel to man has been produced, but the toxicity is believed to be very low. No USPHS limit has been set (McKee & Wolfe, 1961).

Nickel in any concentration is injurious to plants, especially citrus plants, and the problem is heightened in acidic soils (Wilcox, 1959).

Russia has imposed a maximum limit of 1 mg/l in drinking water (Kirkor, 1951).

Nickel concentrations in the Ohio River Basin were generally low (all were below .05 mg/l), and no problems seemed to exist.

Rubidium

Rubidium concentrations throughout the Ohio River Basin were generally quite low, with all values less than .02 mg/l. The concentrations ranged from a high of .015 mg/l to a low of less than .0005 mg/l. The highest concentration came from a Pennsylvanian age source located in Wolfe County, Kentucky. Two wells shared the next highest value, .012 mg/l. One well tapped the Pottsville Fm., Pennsylvanian age, located in Jackson County, Ohio. The other tapped an un-named source in Muhlenburg County, Kentucky. Certainly a problem exists in this last Muhlenburg County well. This well also had maximum values for boron, beryllium, chromium, cobalt, iron, lithium, lead, and nickel. The low value was shared by two wells: a Butler County, Pennsylvania well tapping a Conemaugh Fm., Mississippian age source, and a well tapping an alluvium source in Washington County, Ohio.

The median value for rubidium was .002 mg/l. No source median varied from the overall median by more than .005 mg/l. No trends were obvious.

Rubidium is a highly reactive alkali metal, and is found in nature only in the ionized or combined state. Its salts are highly soluble. There is no evidence of rubidium's toxicity to human beings (Browning, 1961) There is no evidence that it serves any essential metabolic function, but it can be substituted for potassium in some physiological functions.

Silver

Silver possessed a range in values which tended to be both narrow and low.

The highest concentration of silver was less than .006 mg/l and the low was .00006 mg/l. The high came from a well tapping an unstated source in Muhlenburg County, Kentucky. This well possesses maximum values for nine elements. The second highest value, less than .004 mg/l, came from a Pennsylvanian source in Daylight, Indiana. This well had high values for nickel and cobalt. The low value was .00006 mg/l, and came from a well tapping the Pottsville Fm., Pennsylvanian age, in Owls Nest, Pennsylvania. Five other values were below .0001, and it is interesting to note that all came from Pennsylvanian age sources, specifically the Pottsville and Allegheny Fms.

The median for silver was less than .0007 mg/l. This is seven ten thousandths of one part per million. This is a very small amount. The only geologic source medians which were below the overall median were Mississippian and Pennsylvanian age rocks, with their medians both possessing the same value, less than .0002 mg/l. All other source medians were above less than .0007, except the single Tertiary and Cretaceous source which had a value of less than .0001 mg/l. Surely, the overall low values are related to the absence of silver bearing igneous rocks in the Ohio River Basin.

In nature, silver is found in the elemental form and also in silver ores. From these ores, silver may be leached into ground and surface waters. Many silver salts, including the chloride, sulfide, phosphate, and arsenate are insoluble, therefore silver can not be expected to occur in natural waters in significant concentrations (McKee & Wolfe, 1963).

Silver in concentrations of .000001 to .5 mg/l have been reported sufficient to sterilize water (Taumann, 1932). Silver has not been found toxic to man, but in order that its use as a sterilizing agent is not abused, the USPHS has set a limit of .05 mg/l for domestic use (McKee & Wolfe, 1963).

The ingestion of large amounts of silver does not cause toxic symptoms, but does produce bluish permanent darkening of the skin called "argyria."

Silver in the Ohio River Basin does not seem to exist in high enough concentrations to cause problems.

Strontium

Strontium had a very wide range of values throughout the Ohio River Basin. Throughout the entire range of values for all elements sought, strontium had the second highest maximum concentration value, 21 mg/l. The lowest concentration was .0003 mg/l. The high concentration came from a well tapping sand and gravel located in Madison County, Ohio. The three succeeding high values originated from limestone sources. The values were 12 mg/l, 4.1 mg/l, and 2.2 mg/l, and all three came from wells tapping the Bass Island Group, Silurian age, Union County, Ohio, the Niagara Group, Silurian age, Fayette County, Ohio and the Columbus and Delaware Limestone, Devonian age, respectively. The Muhlenburg County, Kentucky well also had a very high value, 3.4 mg/l.

The low value, .0003 mg/l, came from a well tapping the Pottsville Fm., Pennsylvanian age, located in Somerset County, Pennsylvania. The second lowest value came from a Tertiary and Cretaceous source in Carlisle County, Kentucky.

The median value for the entire suite was .260 mg/l and the mean value was 1.003 mg/l.. Four geologic sources had means above the overall mean. They were Niagaran Fm., Silurian, Bass Island Group, Devonian, Columbus and Delaware limestone, Devonian, and sand and gravel. The Pennsylvanian had the lowest source mean, .276 mg/l. The high strontium values for limestone sources could be explained by the association of Celestite, $SrSO_4$, and Barite, $BaSO_4$, which are often associated with Calcite, Siderite, and Dolomite.

The Pennsylvanian rocks, however, might attribute their low value to the fact that the water producing units in the Pennsylvanian are relatively clean sandstones, with the water producing sandstones separated by shales, clays, and siltstones, which might act as aquitards and tend to keep the Pennsylvanian aquifers isolated and relatively uncontaminated.

Traces of strontium are essential in the diet for the formation of bones and teeth. No toxic level has been found for strontium, which has a toxicity similar to calcium. The danger of strontium is in its radioactive isotope, Sr 90, which tends to accumulate in plant material, and hence be concentrated by higher life forms (McKee & Wolfe, 1963).

Tin

Throughout the suite of eighty well samples, eighty tin analysis were performed. The values ranged from a high of less than .080 mg/l to a low of less than .0006 mg/l. The maximum concentration came from a well tapping an unstated source in Muhlenburg County, Kentucky. This well possesses the maximum for ten elements: boron, beryllium, chromium, cobalt, iron, lithium, lead, nickel, second highest for rubidium, and maximum for silver. The next highest value came from a well tapping a Pennsylvanian source located in Daylight, Indiana. This well had high values for nickel, cobalt and silver.

The five lowest values were less than or equal to less than .001 mg/l, with all samples coming from Pennsylvanian age sources, specifically the Allegheny and Pottsville Fms., and with single minimum value, less than .0006 mg/l, coming from the Pottsville Fm.

The median value for tin was less than .010 mg/l. The Mississippian and Pennsylvanian sources were below the median, with both of them having the

same median of less than .003 mg/l. The highest median, less than .013 mg/l, was from the sand and gravel source.

Most tin salts are quite insoluble in water and therefore low concentrations in ground-water can be expected. No reports have been uncovered to indicate that tin can be detrimental in public water supplies. Man can tolerate tin in amounts up to 850 to 1,000 mg/day. Additionally, there is not definite evidence that it plays any essential biological role (Browning, 1961).

Tin in concentrations up to 50 mg/l did not harm stock when ingested from their water supply, and was not harmful to plants when used as irrigation water. Tin, then, exists in quite acceptable concentrations in the Ohio River Basin.

Titanium

Titanium values held consistently low throughout the entire suite of eighty samples. The values ranged from a high of less than .035 mg/l to a low of .0004 mg/l. The high came from an unstated source in Muhlenburg County, Kentucky. The next highest value, less than .025 mg/l, came from a well tapping a Pennsylvanian age source in Daylight, Indiana. The third highest came from the Maxville limestone, Mississippian age, from a well in Wayne County, Ohio. A value of less than .022 mg/l came from a well tapping the Conemaugh Fm., Guernsey County, Ohio.

The lowest concentration, .0004 mg/l, came from a well tapping the Pottsville Fm., Pennsylvanian age. The next lowest value, less than .0006, came from Tertiary and Cretaceous source located in Carlisle County, Kentucky.

The median value of titanium was .006 mg/l. The geologic source medians were all quite close to the overall median for titanium, with all source values being within $\pm$ .006 mg/l to the overall median.

Titanium is quite abundant in the earth's crust and makes up from .5 to .10 percent of soils. It acts as an inert element, similar to silicon in chemical and biological behavior. Many of its salts are highly soluble (McKee & Wolfe, 1963).

There is no evidence that titanium is essential to plant or animal nutrition. It is not absorbed to any large degree by the human intestine, but appears to be inert and innocuous to the human alimentary system (Browning, 1961).

The USPHS and WHO have not set any limits on Titanium concentrations.

Vanadium

Vanadium values were consistently low throughout the entire suite. The values ranged from a high of less than .030 mg/l to a low of less than .0003 mg/l. The high concentration came from two wells, one tapping a sand and gravel source in Trumbull County, Ohio, and the other tapping the Maxville limestone of Mississippian age, located in Wayne County, Ohio. The low was shared by two wells. One tapped the Pottsville Fm., Pennsylvanian age, and was located in Somerset County, Pennsylvania, and the other tapped a Tertiary and Cretaceous source in Carlisle County, Kentucky.

The median value for Vanadium was less than .005 mg/l. The source median values adhered quite closely to the overall median and none were significantly above or below it.

Metallic vanadium does not occur free in nature, but minerals containing vanadium are widespread. Vanadium salts, for the most part, are soluble (McKee & Wolfe, 1963).

Although vanadium does not appear to be essential to nutrition it does seem to have some beneficial effects (Browning, 1961).

According to Mountain (1956), 100 mg/kg of vanadium lowered the cholesterol level in the liver of rabbits, and Stockinger (1960) found that the incidence of coronary disease was lowest in New Mexico, where vanadium concentrations in water are naturally high.

It has also been reported that vanadium in concentrations of .03 to .22 mg/l decreased the amount of dental caries (Tank, 1960).

No drinking water limit has been set by the USPHS. Vanadium occurring in the concentrations found in the Ohio River Basin seem to present no problem.

Zinc

Throughout the eighty wells included in the Ohio River Basin study, nine displayed a very wide range, extending from the highest concentration for any of the trace elements under study, 22.6 mg/l, to a low of non-detectable. The four highest values for zinc, all above 3.3 mg/l, came from three states, Ohio, Kentucky and Pennsylvania, with the highest, 22.6 mg/l, coming from a well tapping the Pottsville Fm. of Pennsylvanian age, located in Somerset County, Pennsylvania. The second highest value, 4.2 mg/l, came from an Ordovician source located in Jessemi County, Kentucky. The third and fourth highest values were less than .9 mg/l and 3.3 mg/l, and both came from Allegheny and Pottsville sources, Pennsylvanian age.

Thirteen samples possessed non-detectable zinc concentrations. Seven were from sand and gravel sources, three from Pennsylvanian sources and three from unstated sources. Sand and gravel seems to possess lower than average zinc concentrations, especially since seven of the nineteen values are non-detectable, however seven of the nineteen values were above the overall median for zinc, .5 mg/l, with the highest zinc concentration for sand and gravel being less than 2.0 mg/l.

The overall median for all eighty zinc samples was .5 mg/l. The Mississippian and sand and gravel source medians were below .5 mg/l. Surprisingly, the Ordovician sources possessed the highest source median, 3.10 mg/l. Accounting for this is difficult. Possibly the Ordovician sources contain zinc minerals such as Sphalerite, Zns. This source is only represented by two samples, however, so generalization is not really possible.

Zinc occurs abundantly in rocks and ores, and has extensive industrial applications. Most zinc salts are soluble, so a high concentration in waste and natural waters might be expected, however some salts, particularly zinc carbonate and zinc sulfate are insoluble, hence much zinc will precipitate and be removed from natural waters (McKee & Wolfe, 1963).

Zinc is essential and beneficial in human nutrition, and a normal diet includes 10-15 mg/day (Browning, 1961). The USPHS has set a limit on zinc of 5 mg/l for domestic use primarily because of its bad taste. At concentrations of 30 mg/l, zinc turns water milky and produces a greasy film on water upon boiling (Kehoe, 1944).

Zinc's most harmful effect is to fish and aquatic life and in soft water. Concentrations of .1 to 1 mg/l have been lethal. Calcium tends to reduce zinc's toxicity (Jones, 1938).

From a human physiological standpoint, all the values found in the Ohio River Basin were well below a toxic level, although a few wells probably produced water which tasted terrible due to zinc concentrations above 5.0 mg/l. However, if the harmful effect of zinc to fish and aquatic life is considered, a problem develops, because fifty of the eighty zinc concentrations were above .1 mg/l, which is the lowest toxic limit to fish in soft water.

Zinc is essential to plant growth, in trace amounts, but when concentrations exceed a very low limit, toxicity results (Kelley & Brown, 1938).

Zirconium

Throughout the range of eighty sample analysis, zirconium yielded a range which was both low and narrow, and which possessed the lowest element median for all 21 elements under discussion, namely a median of non-detectable. The values ranged from a high of less than .060 mg/l to a low of non-detectable. The highest value was shared by two wells, one tapping a sand and gravel source in Trumbull County, Ohio, and the other tapped the Maxville limestone of Mississippian age located in Wayne County, Ohio. The Trumbull County well might possess a problem, because it had near maximum concentrations for several other elements, including barium, boron, beryllium, lithium, nickel, and vanadium. Fourty-one wells possessed the minimum, non-detectable, which was also the median value. The geologic sources which yielded the non-detectable values were varied. In fact, thirteen of the twenty-six separate geologic sources possessed non-detectable as a median value. Zirconium, then, apparently is not abundant even in low concentrations in the Ohio River Basin.

Zirconium chloride, nitrate, and sulfate are soluble in water, however the carbonate, hydroxide, oxide, and silicate are highly insoluble. Therefore, any zirconium which reaches natural waters will be removed by absorption or sedimentation.

Zirconium does not appear to possess a toxic effect to man. Animal studies by Rothstein (1953) indicated that even twenty percent zirconium in oxide animal diets caused no ill effects.

Table of Concentration Values

Minimum, maximum, median and mean concentration values (ug/l) are listed by geologic source. LT means less than, and ND means not detected.

		Aluminum	Barium	Beryllium	Boron	Chromium
For total number of 80 samples	min.	ND	4	LT .2	7	LT .6
	max.	530	770	12	570	LT 40
	med.	25	115	LT 2	51	LT 6
	mean	79	185		86	
Ordovician 2 samples	min.	8	25	LT 2	12	LT 2
	max.	13	25	LT 2	21	LT 7
	med.	11	25	LT 2	17	LT 4.5
	mean	11	25		17	
Silurian Niagaran 3 samples	min.	15	35	LT .4	18	LT .8
	max.	50	160	LT 3	75	LT 7
	med.	40	110	LT 2	23	LT 3
	mean	35	102		39	
Devonian Columbus and Delaware 1 sample		40	55	LT .6	85	LT 2
Bass Island 1 sample		40	4	LT 1	340	LT 2
Mississippian Ponoco 3 samples	min.	10		LT .3	63	LT 2
	max.	230	400	LT 2	66	LT 8
	med.	150	220	LT .4	65	LT 2
	mean	113	212		65.7	
Mississippian undivided 4 samples	min.	9	55	LT .4	20	LT .7
	max.	64	330	LT 4	40	LT 7
	med.	18	190	LT 2	30	LT 6
	mean	25	191		30	
Mississippian Maxville limestone 1 sample		6	32	LT 6	60	LT 23

		Aluminum	Barium	Beryllium	Boron	Chromium
Conneaunt 1 sample		200	68	LT .6	110	LT 3
Cuyahoga 1 sample		ND	30	LT 4	180	LT 20
2 samples		17 27 22 22	15 40 28 28	LT .2 LT 2 LT 1.1	7 9 8 8	LT 3 LT 4 LT 3.5
Mississippian total 11 samples	min. max. med. mean	ND 230 25 104.8	15 400 60 106	LT .2 LT 4 LT 2	7 180 40 78.7	LT .2 LT 20 LT 4
Pennsylvanian	min. max. med. mean	6 440 140 145	17 770 140 276	LT .2 LT 3 LT .5	7 95 43 48	1 LT 15 3
Allegheny 4 samples	min. max. med. mean	130 300 185 200	50 220 140 125	LT .2 LT .7 LT .3	25 85 35 39.6	LT 1 10 LT 25
Conemaugh 7 samples	min. max. med. mean	20 530 150 185	60 340 150 173	LT .3 LT 6 LT 1	25 85 45 48	2 LT 22 LT 6
Dunkard 1 sample		35	150	LT 5	65	LT 13
Pennsylvanian undivided 5 samples	min. max. med. mean	8 15 12 11.6	20 330 95 125	LT .8 LT 8 LT 3	24 450 360 273	LT 3 LT 25 LT 10
Allegheny and Pottsville 3 samples	min. max. med. mean	ND 30 6 15	30 420 420 290	LT .5 LT 5 LT 22	120 140 130 130	LT 1 LT 20 LT 9
Pennsylvanian total 29 samples	min. max. med. mean	ND 530 35 98.6	17 770 150 157	LT .2 LT 8 LT .7	7 450 60	LT 1 LT 25 3

		Aluminum	Barium	Beryllium	Boron	Chromium
Tertiary and Cretaceous 1 sample		6	14	LT .2	10	LT .6
Sand and Gravel 19 samples	min.	5	22	LT .4	7	LT .7
	max.	150	760	LT 12	530	LT 30
	med.	20	110	LT 3	45	LT 7
	mean	31	200		92	
Alluvium 3 samples	min.	30	25	LT .6	15	LT 3
	max.	350	110	LT 5	73	LT 30
	med.	330	27	LT 3	43	LT 6
	mean	237	54		43.6	
Glacial drift 1 sample		27	550	LT 5	91	1
Glacial gravel 2 samples	min.	ND	70	LT 3	30	LT 9
	max.	20	380	LT 4	120	LT 13
	med.	10	225	LT 3.5	75	LT 11
	mean	15	225		75	
No source stated 6 samples	min.	8	30	LT 1	10	LT 4
	max.	250	870	LT 12	570	LT 40
	med.	31	35	LT 2	28.5	LT 9
	mean	67	273		117	

		Cobalt	Copper	Iron	Lead	Lithium	Manganeese
For total	min.	LT .6	LT 1	4	1	.1	.4
number of	max.	LT 80	440	11,000	30	95	3,600
80 samples	med.	LT 8	4	230	LT 5	6	60
	mean					11.4	
Ordovician	min.	LT 11	7	20	LT 4	.8	6
2 samples	max.	LT 13	14	25	LT 4	3	800
	med.	LT 12	10.5	22.5	LT 4	1.9	403
	mean		10.5	22.5		1.9	403
Silurian	min.	LT 4	LT .8	30	LT 5	3	LT 3
Niagaran	max.	LT 15	LT 7	680	13	9	170
3 samples	med.	LT 14	LT 3	60	5	5	22
	mean			256			
Devonian Columbus and Delaware 1 sample		LT 6	50	200	30	13	26
Bass Island 1 sample		40	6	3,800	LT 8	90	60
Mississippian	min.	.8	2	140	2	7	2
Ponoco	max.	8	4	2,400	11	15	230
3 samples	med.	2	2	860	LT 8	13	190
	mean	3.6	2.7	1,133		11.6	140.6
Mississippian	min.	LT 4	1	75	LT 3	.3	8
undivided	max.	LT 12	11	1,300	LT 7	11	240
4	med.	LT 6	3	225	LT 4	6	102
	mean		4.5	456		7.7	113
Maxville limestone 1 sample		LT 23	LT 5	LT 1,500	LT 23	30	340
Conneaunt 1 sample		2	3	450	4	6	29
Cuyahoga 1 sample		LT 20	LT 4	90	LT 20	26	75
Mee.	min.			13	LT 4		5
2 samples	max.			30	LT 5		10
	med.	LT 4	3	21	LT 4.5	1	7.5
	mean			22			7.5

		Cobalt	Copper	Iron	Lead	Lithium	Manganeese
Mississippian	min.	.8	1	13	2	.3	2
total	max.	LT 12	11	2,400	11	26	240
11 samples	med.	LT 4	3	140	4	7	65
	mean			430		8.4	90.3
Pennsylvanian	min.	.8	1	4	3	1	.6
Pottsville	max.	LT 15	15	4,000	29	21	560
9 samples	med.	LT 4	4	970	4	7	72
	mean		6			7.9	
Allegheny	min.	.6	3	1,100	3	1	210
4 samples	max.	2	9	2,300	5	14	580
	med.	.9	4.5	1,700	3.5	7.5	340
	mean	1.1	5.2			7.5	367
Conemaugh	min.	.8	LT 3	19	2	2	3
7 samples	max.	LT 22	11	LT 3,000	LT 22	15	680
	med.	3	4	230	5	5	270
	mean	5				5.9	237
Dunkard		10	3	1,000	LT 8	8	1,000
1 sample							
Pennsylvanian	min.	LT 5	LT 2	5	1	9	6
undivided	max.	LT 50	25	70	LT 15	35	25
5 samples	med.	10	7	25	LT 10	20	23
	mean			27.6		21	
Allegheny and	min.	LT 5	LT 2	30	LT 4	11	12
Pottsville	max.	LT 20	7	2,400	LT 20	35	620
3 samples	med.	9	5	120	LT 9	14	16
	mean			850		20	216
Pennsylvanian	min.	.6	1	4	1	1	.6
total	max.	LT 50	25	4,000	29	35	1,000
29 samples	med.	8	4	970	5	8	72
	mean					9	
Tertiary and Cretaceous		LT 2	440	5	4	.1	.4
1 sample							
Sand and	min.	LT 4	1	10	2	2	.8
Gravel	max.	LT 25	250	4,500	LT 20	90	3,600
19 values	med.	LT 12	6	490	LT 3	5	45
	mean			947	LT 4	12.3	

		Cobalt	Copper	Iron	Lead	Lithium	Manganeese
Alluvium	min.	2	2	25	LT 2	.2	8
3 samples	max.	20	10	3,400	LT 16	20	2,200
	med.	5	5	69	LT 4	4	120
	mean	9	9	1,165		8.1	747
Glacial drift 1 sample		2	1	210	LT 2	37	120
Glacial gravel	min.	7	2	110	LT 5	5	22
2 samples	max.	13	LT 3	130	LT 13	7	40
	med.	10	LT 2.5	120	LT 9	6	31
	mean			120		6	31
No source	min.	LT 7	2	8	3.3	2	2
stated	max.	LT 80	5	11,000	LT 2	95	490
	med.	LT 11.5	4	495	LT 25	6	43
	mean		3.3	2,404	LT 9	21.3	

		Molybdenum	Nickel	Rubidium	Silver	Strontium
For total number of 80 samples	min.	.1	.7	.5	.06	.3
	max.	37	40	15	6	21,000
	med.	5	6	2	.7	260
	mean					1,003
Ordovician 2 samples	min.	LT 1	LT 6	LT 2	LT .8	130
	max.	1	11	2	LT 1	260
	med.	1	LT 8.5	LT 2	LT .9	195
	mean					195
Silurian Niagaran 3 samples	min.	1	LT 2	LT 3	LT .4	240
	max.	11	LT 8	2	LT 1	4,100
	med.	9	LT 7	LT 2	LT 1	1,100
	mean	6.6				1,088
Devonian Columbus and Delaware 1 sample		8	10	LT 3	LT .6	2,200
Bass Island 1 sample		23	LT 4	LT 4	LT 1	12,000
Mississippian Ponconо 3 samples	min.	LT .3	3	1	LT .1	89
	max.	LT 2	LT 6	11	LT 1	260
	med.	LT .6	3	2	LT .1	100
	mean			3.2		149
Mississippian undivided 4 samples	min.	LT .7	1	LT 1	LT .2	LT 10
	max.	4	LT 6	2	LT 1	1,300
	med.	LT 1.5	LT 2	1	LT .2	550
	mean					610
Maxville limestone 1 sample		LT 6	LT 18	LT 7	LT 3	330
Conneaunt 1 sample		4	2	.6	LT 2	210
Cuyahoga 1 sample		16	LT 17	LT 3	LT 2	2,100
Mee. 2 samples	min.	LT .7	LT .7	LT 1	LT .2	310
	max.	LT .9	2	1	LT .2	680
	med.	LT .8	LT 1.3	LT 1	LT .2	495
	mean					495

		Molybdenum	Nickel	Rubidium	Silver	Strontium
Mississippian total 11 samples	min.	LT .3	LT .7	LT 1	LT .1	40
	max.	16	17	11	LT 2	2,100
	med.	1	3	1	LT .2	310
	mean					563
Pennsylvanian Pottsville 9 samples	min.	LT .1	LT .7	.5	LT .06	.3
	max.	LT 6	14	9	LT 2	870
	med.	LT .7	3	2	LT .2	130
	mean					312
Allegheny 4 samples	min.	LT .2	1	1	LT .06	31
	max.	LT .6	5	3	.2	130
	med.	LT .2	3.5	2	LT .13	44
	mean		3.2	2		62
Conemaugh 7 samples	min.	LT .5	LT 2	LT .5	.1	57
	max.	LT 5	LT 17	LT 7	LT 3	800
	med.	LT 3	4	LT 2	LT .3	180
	mean					276
Dunkard 1 sample		LT 3	LT 8	LT 1	LT 2	480
Pennsylvanian 5 samples	min.	LT .8	LT 3	LT 4	LT .4	30
	max.	LT 4	LT 25	15	LT 4	820
	med.	LT 1	LT 7	5	LT 2	210
	mean					296
Allegheny and Pottsville 3 samples	min.	LT 2	LT 4	LT 3	LT .5	230
	max.	LT 9	LT 17	12	LT 2	630
	med.	LT 2	LT 6	9	LT 1	540
	mean					350
Pennsylvanian total 29 samples	min.	LT .1	LT .7	LT .5	.06	.3
	max.	LT 9	LT 25	15	LT 4	870
	med.	LT 1	4	LT 3	LT .2	180
	mean					286
Tertiary and Cretaceous 1 sample		LT .2	2	.6	LT .1	5
Sand and gravel 19 samples	min.	.5	LT 2	.5	LT .07	23
	max.	37	LT 20	6	LT 3	21,000
	med.	LT 4	LT 7	LT 2	LT 1	240
	mean					1,432

		Molybdenum	Nickel	Rubidium	Silver	Strontium
Alluvium	min.	LT .6	1	LT .5	LT .2	65
3 samples	max.	LT 6	LT 10	LT 6	LT 2	880
	med.	LT 2	LT 4	LT .7	LT .6	96
	mean					347
Glacial drift 1 sample		3	1	.4	LT .1	140
Glacial	min.	LT 2	LT 5	1	LT .9	130
gravel	max.	22	LT 11	LT 2	LT 2	420
2 samples	med.	LT 10	LT 8	LT 1.5	LT 1.5	275
	mean					275
No source	min.	LT 2	4	.7	LT .5	35
stated	max.	21	LT 40	12	LT 6	3,400
6 samples	med.	LT 9	LT 7	2	LT .9	235
	mean			3.8		813

		Tin	Titanium	Vanadium	Zinc	Zirconium
For total number of 80 samples	min.	.6	.4	LT .3	ND	ND
	max.	80	25	30	22,600	60
	med.	3	6	5	500	ND
	mean					
Ordovician 2 samples	min.	LT 11	LT 4	LT 3	2,000	ND
	max.	LT 13	LT 6	LT 4	4,200	ND
	med.	LT 12	LT 5	LT 3.5	3,100	ND
	mean					
Silurian Niagaran 3 samples	min.	LT 8	3	LT 4	110	ND
	max.	LT 15	LT 6	LT 8	LT 600	ND
	med.	LT 14	LT 5	LT 4	600	ND
	mean					
Devonian Columbus and Delaware 1 sample		LT 12	LT 6	LT 12	LT 60	ND
Bass Island Silurian 1 sample		LT 20	LT 10	LT 20	LT 100	ND
Mississippian Ponoco 3 samples	min.	LT 2	LT 4	LT .8	75	LT 2
	max.	LT 12	11	LT 10	1,300	LT 20
	med.	LT 2	4	LT 1	LT 570	LT 2
	mean					
Mississippian undivided 4 samples	min.	LT 2	1	LT 3	LT 20	ND
	max.	LT 12	LT 6	LT 7	270	ND
	med.	LT 2	LT 3	LT 5.5	LT 35	ND
	mean					
Maxville limestone 1 sample		LT 35	LT 23	LT 30	2,200	LT 60
Conneaunt 1 sample		LT 3	7	LT 2	LT 90	LT 3
Cuyahoga 1 sample		LT 20	LT 17	LT 20	860	ND
Mee. 2 samples	min.	LT 2	.6	LT 4	LT 60	ND
	max.	LT 2	3	LT 5	360	ND
	med.	LT 2	1.8	LT 4.5	210	ND
	mean					

		Tin	Titanium	Vanadium	Zinc	Zirconium
Mississippian total 11 samples	min.	LT 2	6	LT .8	LT 20	ND
	max.	LT 20	11	LT 20	2,700	LT 20
	med.	LT 3	5	LT 4	LT 90	ND
	mean					
Pennsylvanian Pottsville 9 samples	min.	LT .6	.4	LT .3	ND	ND
	max.	LT 16	16	LT 15	22,600	LT 2
	med.	LT 2	LT 7	LT 4	LT 290	LT 1
	mean					
Allegheny 4 samples	min.	LT 1	4	LT .5	210	LT 1
	max.	LT 3	11	LT 2	2,700	LT 3
	med.	LT 1	7	LT 5.5	600	LT 1
	mean		7.2			
Conemaugh 7 samples	min.	LT 2	LT 2	LT .8	110	ND
	max.	LT 35	LT 22	LT 27	1,100	LT 55
	med.	LT 7	6	LT 3	370	LT 6
	mean					
Dunkard 1 sample		LT 15	LT 8	LT 13	LT 750	LT 25
Pennsylvanian undivided 5 samples	min.	LT 5	LT 3	LT 2	ND	ND
	max.	LT 50	LT 25	LT 17	LT 970	LT 35
	med.	LT 14	LT 10	LT 12	210	ND
	mean					
Allegheny and Pottsville 3 samples	min.	LT 10	LT 5	LT 10	LT 610	ND
	max.	LT 20	LT 17	LT 20	3,900	LT 20
	med.	LT 13	LT 9	LT 10	3,300	ND
	mean					
Pennsylvanian total 29 samples	min.	LT .6	.4	LT .3	ND	ND
	max.	LT 50	LT 25	LT 27	22,600	LT 55
	med.	LT 3	LT 5	LT 4	370	LT 2
	mean					
Tertiary and Cretaceous 1 sample		LT 2	LT .6	LT .3	110	ND
Sand and gravel 19 samples	min.	LT 2	LT 3	LT 1	ND	ND
	max.	LT 35	LT 20	LT 30	LT 2,000	LT 60
	med.	LT 13	LT 6	LT 4	45	ND
	mean					

		Tin	Titanium	Vanadium	Zinc	Zirconium
Alluvium	min.	LT 3	LT 4	LT 2	LT 95	LT 3
3 samples	max.	LT 27	LT 11	LT 14	LT 800	LT 27
	med.	LT 7	4	LT 6	LT 350	LT 12
	mean					
Glacial drift		LT 3	9	LT 1	LT 70	LT 3
1 sample						
Glacial	min.	LT 10	LT 5	LT 9	LT 250	ND
gravel	max.	LT 13	LT 11	LT 13	LT 500	LT 17
2 samples	med.	LT 13	LT 8	LT 11	LT 325	LT 9
	mean					
No source	min.	LT 7	LT 3	LT 2	ND	ND
stated	max.	LT 80	LT 35	LT 20	850	LT 30
6 samples	med.	LT 9	LT 7	LT 9	LT 90	ND
	mean					

CONCLUSIONS

The trace element study performed by the U.S.G.S. has suggested at least four things: that certain of the sample wells tended to produce high concentration values, that certain geologic sources tended to produce high concentrations, that certain geologic sources tended to produce low concentrations, and that problem concentrations do exist, at least for some elements.

One well of unstated source in Muhlenburg County, Kentucky produced maximum concentrations for eleven elements: boron, beryllium, chromium, cobalt, iron, lithium, nickel, rubidium, silver, tin and titanium. The dissolved solids of that well were three thousand, eight hundred and seventy ppm. This is the highest dissolved solids of any of the eighty wells. It is very possible that this well is contaminated. Another well, tapping a sand and gravel source in Trumbull County, Ohio and possessing a dissolved solids value of two thousand, six hundred ppm. yielded maximum concentrations for boron, beryllium, nickel, vanadium, and zirconium. Contamination of this well is possible. The U.S.P.H.S. limit for dissolved solids is five hundred ppm. What the above data suggests is that some wells have high trace element concentrations not because of a specific geologic source, but because they are possibly contaminated. Certainly, though, geologic source is related to contamination. A sand and gravel source, with high permeability, rapid ground water movement, and relative shallowness, for example, could easily be contaminated.

One geologic source showed consistently high median concentrations, namely wells tapping sand and gravel. For 14 of the 21 elements, the sand and gravel median equalled or exceeded the median for the total number of samples. The fourteen elements were barium, beryllium, boron, chromium, cobalt, copper,

iron, lithium, nickel, silver, titanium, rubidium, vanadium and tin.

The Pennsylvanian sources, specifically the Pottsville and Allegheny Fms., produced low values. The Pottsville sources produced minimums for 11 elements including vanadium, cobalt, strontium, boron, iron, manganeese, aluminum, silver, zinc, titanium and copper. In addition, 13 of 21 medians for Pottsville sources were below the element medians for all eighty samples. The Pottsville aquifers, then, appear to be producing water of good relative quality. The Pottsville Fm. is two hundred and forty feet thick and consists of thick sandstones alternating with shales and coals. The thin shales and coals might act as aquacludes and tend to keep the sandstone aquifers free from contamination. The sandstone itself consists mainly of quartz (silica) sand and would not produce highly mineralized water. However, the Pottsville Fm. did possess high concentrations of iron.

Concentrations at problem levels did exist for some elements. The biggest problems were iron and manganeese. Iron exceeded the USPHS limit of .3 mg/l in forty of eighty wells sampled. Forty-two of eighty wells surpassed the USPHS limit for manganeese, .05 mg/l. The sources which produced the highest concentrations of these two elements were sand and gravel sources and aquifers of Pennsylvanian age (see element discussion for iron).

Zinc surpassed the limit of 5. mg/l in one case and approached the limit several times. Twelve zinc values were 1.0 mg/l or greater.

Strontium had high values (one value was 21 mg/l) but poses no known threat to domestic or irrigation use.

In addition, copper, chromium and lead closely approached their USPHS limits. The limit for copper is 1 mg/l and the copper maximum was .440 mg/l. The limit for chromium is .05 mg/l and the maximum chromium concentration was .040 mg/l. Lead has a limit of .05 mg/l, and the highest lead value was .03 mg/l.

Hopefully this report will be used as a tool to better understand the abundance or rarity of the major as well as the minor trace elements in groundwaters throughout the Ohio River Basin and their implications to domestic, industrial and agricultural water use.

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